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TITLE:

**Low Volatility Formulations of
Microencapsulated Clomazone**

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LOW VOLATILITY FORMULATIONS OF
MICROENCAPSULATED CLOMAZONE

5 589 This is a continuation-in-pad of Ser. No. 340,699, filed
Nov. 16, 1994, abandoned.

10 509 The present invention relates to formulations of cloma-
zone having reduced volatility relative to conventional
emulsifiable concentrates of clomazone. In particular it
relates to microencapsulated formulations of clomazone in
which the clomazone is encapsulated in a shell of polyurea.

15 Clomazone, the common name for 2-(2-chlorophenyl)
methyl-4,4-dimethyl-3-isoxazolinone, a highly effective
herbicide, is also highly volatile, so much so that clomazone
applied to the soil in a target area may move to adjacent area
s and there cause discoloration, most typically whitening or
some degree of bleaching, of a variety of crops, trees, or
decorative plants. While this bleaching, indicative of the
mode of action of the herbicide, may be temporary when
plants are exposed to sufficiently low concentrations, it is
20 unwelcome, even when it does not result in the destruction
of the plant. Accordingly, the label for the use of Com-
mand® 4 EC Herbicide, an emulsifiable concentrate formu-
lation in commercial use that contains four pounds of
clomazone per gallon of formulation, lists a number of
25 restrictions on how the product is to be used, including
weather conditions, spray volume and pressure, and distance
from areas where plants are in commercial production. For
example, for preemergent applications clomazone is not to
be applied, within 1,500 feet of commercial fruit, nut, or
vegetable production or commercial greenhouses or nurser-
ies. Clearly, this is a severe limitation on the use of an
herbicide.

30 It is the purpose of the present invention to reduce the
volatility of clomazone formulations, so that problem of
off-site injury is significantly reduced, i.e., by at least fifty
percent, while maintaining a satisfactory level of herbicidal
activity in the target area.

35 Attempts to prepare formulations of encapsulated clo-
mazone by the general methods known to the art, including
polyamide shells as well as polyurea, frequently resulted in
formulations that not only gave little or no reduction in
volatility, but had poor physical characteristics, e.g., unde-
sirable agglomeration of the capsules or separation of
phases. Perhaps one factor accounting for the difficulty in
40 preparing satisfactory formulations is the significant water
solubility of clomazone. No reports of formulations of
encapsulated clomazone have been found.

45 It has now been found that encapsulated formulations of
clomazone for which the volatility is reduced to fifty percent
or less than that of the commercially available Command®
4 EC emulsifiable concentrate of clomazone, and which
retain a satisfactory level of herbicidal activity, can be
prepared, provided that the isocyanate and amine moieties
that are to form the polyurea shell wall are carefully
50 selected.

55 The process of the invention involves the following
steps: (a) providing an aqueous phase containing an emul-
sifier, preferably a partially hydrolyzed polyvinyl alcohol; an
antifoam agent, and optionally a xanthan gum viscosity
modifier/stabilizer; (b) providing a water immiscible phase
60 consisting of clomazone and polymethylene polyphenyl
isocyanate, with or without a hydrocarbon solvent; (c)
emulsifying the water immiscible phase in the aqueous
phase to form a dispersion of water-immiscible droplets
throughout the aqueous phase; (d) agitating the dispersion
65 while adding to it, either neat or in aqueous solution,
ethylenediamine, diethyluramine, triethylenetetramine, 1,6-

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hexanediamine, or a mixture of the polyfunctional amines, thus forming a polyurea shell wall around the water-immiscible droplets. Once the microcapsules are formed, the suspension is cured by moderate heating, after which one or more stabilizing agents, such as propylene glycol, xanthan gum, smectite clay, or an ionic dispersing agent such as a sulfonate of an alkyl naphthalene, may be added, as is well-known in the art. It has also been found that adjusting the pH of the formulation from mildly acidic to mildly alkaline conditions, such as a range of from 6.5 to 9.0, e.g., pH 8.9, results in a formulation having improved storage stability. The addition of these materials after encapsulation and curing to adjust viscosity and suspensibility is not seen to have any effect on the loss of clomazone through volatility or on the herbicidal efficacy of the formulation.

The aqueous phase will ordinarily contain 0.3 to 3.0, preferably 0.8 to 2.0, weight percent of one or more emulsifiers, e.g., polyvinyl alcohol, 0.05 to 0.20, preferably 0.06 to 0.15, weight percent of the xanthan gum viscosity modifier/stabilizer, if it is used, and 0.1 to 1.0, preferably 0.4 to 0.9, weight percent of the antifoam agent.

The water-immiscible phase will ordinarily consist of 60 to 85, preferably 65 to 77, weight percent of clomazone, an amount of polymethylene polyphenyl isocyanate (PMPPi) such that the ratio of clomazone to PMPPi is in the range of 1:1 to 6:1, preferably 4.5:1 to 4.8:1, and an aromatic hydrocarbon solvent for the two solutes. However, use of solvent is optional in the preparation of formulations containing more than about two pounds of clomazone per gallon of formulation. In such preparations a small amount of solvent may still be used to depress the melting point.

The amine solution will ordinarily contain 10 to 100, preferably 30 to 40, weight percent of ethylenediamine, diethylenetriamine, triethylenetetramine, 1,6-hexanediamine, or preferably a mixture of the polyfunctional amines, with ethylene diamine being used only in a mixture.

The emulsification step requires high shear mixing to give small droplets of the immiscible phase. Factors that influence droplet size, which determines the eventual size of the microcapsules, as well as the stability of the emulsion, include speed and length of mixing, the type and amount of surfactant, solvent, temperature, and viscosity, as well as the xanthan gum, when used. Selection of the appropriate microcapsule size to achieve the purposes of the invention requires a balance between competing factors. In general, increasing microcapsule size decreases volatility, but also decreases suspensibility of the particles, while decreasing size yields better suspensibility, but higher volatility. For the purposes of the present invention the average size of the microcapsules is 5 to 50 microns, preferably 5 to 30 microns. The operating conditions to yield microcapsules of a desired size will depend on the emulsifying equipment used, and the adjustment to determine the proper conditions is well within the skill of the art.

In contrast to the conditions of the emulsification step, agitation during the amine addition should be gentle. Stirring is continued while the suspension is cured by heating to a temperature of 35 to 60, preferably 45° to 50° C., for 3 to 10, preferably 4 to 5, hours.

The amounts of post encapsulation additives to be added typically would be selected from one or more of 0.75 to 6.5 wt. % propylene glycol, 0.05 to 0.30 wt. % xanthan gum, 0.25 to 0.50 wt. % smectite clay, and 0.5 to 6.0 wt. % one or more surfactants, each weight percent relative to the weight of the formulation after addition of the stabilizers.

The formulations of the present invention are prepared by the methods exemplified in the following examples.

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DE EXAMPLE 1

Preparation of a Clomazone 1.5 Pound/Gallon
Capsule Suspension (5 CS) Formulation
(Formulation A).

A stock solution of aqueous 20% (weight/weight) partially hydrolyzed polyvinyl alcohol having an average molecular weight of 13,000 to 23,000 (Airvol® 203) was prepared by stirring and heating the appropriate amounts of polyvinyl alcohol and water at about 80°-90° C. for one hour. The cooled solution was stored for later use.

In a one-liter stainless steel beaker were placed 20.0 grams of the aqueous 20% polyvinyl alcohol solution prepared above, 1.8 grams of 100 % of a polydimethyl siloxane antifoam agent (Dow Corning® 1500), 15.0 grams of aqueous 2% xanthan gum (Kelzan® M), and 400.0 grams of water. After this mixture was mixed for 20 seconds at high speed in a high-shear mixer, a pre-blended solution of 140.0 grams of clomazone, 30.0 grams of polymethylene polyphenyl isocyanate (PMPPi, Mondur® MR), and 30.0 grams of petroleum solvent (a mixture of C₉-C₁₅ aromatic naphthalene-depleted hydrocarbons, flash-point 95° C., Aromatic 200 ND) was added, and the mixture was emulsified in the high shear mixer for five minutes. The mixture was then placed in a one-liter jacketed resin flask with the jacket pre-heated to 50° C. The mixture was stirred at a moderate speed with an air-powered stirrer, and a solution of 19.0 grams of triethylenetetramine (TETA) in 35.0 grams of water was added in one portion. The mixture was then stirred at 50° C. for four hours. After this time, 2.5 grams of a smectite clay containing magnesium aluminum silicate, titanium dioxide, and cristobalite (Veegum® Ultra), and 15.0 grams of aqueous 2% xanthan gum (Kelzan® M) were added to stabilize the formulation. The formulation was then stirred for about one hour and stored for later use.

The formulations described in Tables 1 and 2 were prepared in this manner.

EXAMPLE 2

Large Scale Preparation of a Clomazone 2.0
Pound/Gallon Capsule Suspension (2.0 CS)
Formulation (Formulation E-1)

A solution of 5.24 pounds of polyvinyl alcohol (Airvol 203), 2.38 pounds of an aqueous solution of 20% polydimethyl siloxane antifoam agent (Dow Corning® 1520), and 0.21 pound of xanthan gum viscosity modified/stabilizer (Kelzan® S) in 284.20 pounds of water was placed in a 500 gallon stainless steel vessel, and stirred at 80° C. for one hour. After this time the solution was cooled to 20° C. and placed in an 80 gallon batch homogenizer. With the homogenizer in operation, a pre-blended solution of 161.34 pounds of technical clomazone, 34.75 pounds of polymethylene polyphenyl isocyanate (PMPPi, Mondur® MR), and 34.75 pounds of petroleum solvent (a mixture of C₉-C₁₅ aromatic hydrocarbons, flash-point 95° C., Aromatic 200) was fed by gravity into the homogenizer during a 15 to 90 second period. The mixture was homogenized for two to three minutes. Upon completion of the homogenization, the mixture was placed in a jacketed reactor with the jacket pre-heated to 50° C. To the jacketed reactor was added, over a period of 30 seconds, an amine mixture consisting of 10.97 pounds of triethylenetetramine (TETA) and 10.97 pounds of 1, 6-hexanediamine (HDA). After the amine addition was completed, the mixture was cured with agitation at 25° C. to

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That attaining the desired combination of reduced volatility, physical properties, and efficacy is not achieved simply by following the prior art is shown by two additional preparations. Formulations V and W were prepared by the method of U.S. Pat. No. 4,280,833, Example 8. The composition of these formulations is given in Table 5a. Both formulations separated on standing, forming in the bottom of the container a hard-packed layer, which could be redispersed by shaking. Each gave at least as much release of clomazone as the standard Command® 4 EC Herbicide, when subjected to the laboratory volatility test described below.

The average size of the microcapsules of formulations of the invention, as well as the unsatisfactory formulations, is given in Table 6.

Volatility Studies

Laboratory tests for the volatility of capsule suspension (CS) formulations of clomazone were carried out in the following manner. Sufficient unsterilized topsoil to conduct the test was passed twice through a 14-mesh sieve to remove large particles and debris. The fine particles were then removed through a 30-mesh sieve, leaving behind topsoil of intermediate-sized particles. This intermediate-sized topsoil, 240 grams, was spread uniformly to a thickness of about one to two millimeters over an area of about 27.9 cm x 41.3 cm in a tray measuring 32.4 cm x 45.7 x 1.9 cm. The topsoil was then sprayed from an overhead track sprayer calibrated to deliver 20 gallons of water per acre. The spray mix consisted of sufficient clomazone test formulation to provide 0.0712 gm of active ingredient in 20 mL of water. In this manner the clomazone test formulation was applied to the soil at a rate of 1.0 kg a.i. (active ingredient)/ha. Immediately after treatment, the soil was enclosed in a glass jar, where it remained briefly until used.

For each clomazone test formulation, four 22 mm x 300 mm glass chromatography columns, each containing a coarse sintered glass barrier at the bottom, were connected through their bottom ends to a multi-port air manifold, which delivered equal air pressure simultaneously to a number of columns. In each of the four columns was placed 59 gms of the treated topsoil, which filled about 200 mm of the column length. In the top of each column was then placed a polyurethane foam plug designed to fit inside a 21 to 26 mm diameter tube. As soon after the soil treatment as the columns could be set up, a slow stream of air (0.75-1.00 liter per minute per column) from the multi-port air manifold was passed through the soil in each column, causing the volatilized clomazone to collect on the polyurethane foam plug. The time between the soil treatment and the start of the air flow was about one hour. The air flow was continued for about 18 hours.

Following the 18 hour collection period, the polyurethane foam plug from each column was placed in a 20 mL plastic syringe. The polyurethane foam plug was thoroughly extracted by drawing 15 mL of methanol into the syringe and through the plug, forcing the methanol extract into a beaker, and repeating the process several times. A 0.04 mL aliquot of the 15 mL sample was diluted with 0.96 mL of methanol and 1.0 mL of water. A 0.1 mL aliquot of this solution was analyzed for clomazone content using an enzyme-linked immunosorbent assay (ELISA), a method reported by R. V. Darger et al. (J. Agr. and Food Chem., 1991, 39, 813-819). The total clomazone content of the foam plug, expressed in micrograms, of each sample was

recorded and compared to the clomazone content of the sample from the standard, Command® 4 EC Herbicide.

The test results, given in Table 7, show that the CS formulations of the present invention are effective in reducing the amount of clomazone lost by volatility. While all of the formulations listed gave a significant reduction in volatility, the results for Formulations E and F, prepared from mixtures of TETA and HDA, are particularly noteworthy, losing only 8% and 10%, respectively, as much clomazone as was lost from the standard 4 EC. The 2.0 lb/gal formulations made from the single polyfunctional amines, Formulation B from TETA and Formulation D from HDA, each lost more than twice as much clomazone as did the formulations prepared from mixtures. Also, Formulations G and H each had less volatility loss than that of either HDA or DETA alone (Formulations J and K). Accordingly, in the preparation of the formulations of this invention, the use of mixtures of DETA or TETA or both with HDA, particularly in ratios of 3:1 to 1:3, give unexpectedly superior reduction of volatility. Mixtures of TETA and EDA give volatility lower than that of TETA alone. However, it should be noted that Formulation P, a 3 lb/gal formulation, with DETA alone, gave as much reduction in volatility as Formulations G and H.

The unsatisfactory formulations L, M, and N are clearly far less effective in reducing the volatility of clomazone. The high volatility loss for Formulation L (91% of that lost by the standard clomazone 4.0 EC) suggests that the polymeric walls formed from triethylenetetramine (TETA) and TDI are too permeable, allowing the clomazone to volatilize and the walls formed from PMPPI and TETA or PMPPI in combination with TETA and 1,6-hexanediamine (HDA) are much less permeable, so that clomazone loss from volatility is much reduced. Formulation M, which gives excellent results when the active ingredient is a less water-soluble insecticide, is totally unacceptable for clomazone, giving volatility equal to that of the standard clomazone 4.0 EC. The difference between Formulations A and N in reducing the loss of clomazone through volatility is particularly surprising, inasmuch as the only difference is the absence of xanthan gum in the aqueous solution prior to encapsulation in Formulation N. The function of xanthan gum seems unpredictable, however, since the only difference between Formulations K and O is the presence of xanthan gum in the aqueous solution prior to encapsulation in K. These two formulations have the same volatility loss, but the viscosity of Formulation K is 3640 cps, while that of O is 6360. No discernible difference has been found between Kelzan® M and Kelzan S xanthan gum in the aqueous phase prior to encapsulation in their effect on the formulations.

Formulations V and W, based on the an earlier patent, were no better than the 4 EC formulation in controlling volatility.

Tests to determine the volatility of clomazone CS formulations in the field relative to that of the standard, Command® 4 EC Herbicide, were carried out as follows. One trial on Formulation A-1 was conducted in a field of two-week old sunflowers, a plant species susceptible to clomazone. Plots were established on a 12x14 meter grid. Each plot was prepared by removing the sunflower seedlings and other vegetation from areas about 60 cm in diameter located at the intersections of the grid lines. The grid lines were 12 meters apart in one direction, and 14 meters apart in the perpendicular direction. The edge of one replicate was at least 12 meters from the edge of the next replicate, a distance sufficient to prevent interference between replicates. Over each plot where the soil was exposed was placed a 60 cm

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diameter, open-ended barrel that was lined with a plastic sleeve fashioned from a trash can liner. Each plot was sprayed with 10-15 mL of an aqueous dispersion containing 0.12 gram of active ingredient. To minimize the drift of clomazone, the spraying was conducted inside the barrel using a hand-held sprayer. Upon completion of each application, the barrel was left in place, and the top was covered for about two to three minutes to allow the spray to settle to the soil surface. The barrel was then removed, leaving each plot open to ambient conditions. There were three to four replicates for each test formulation. To prevent cross-contamination, the plastic sleeve was replaced before applying each new test formulation. The test was evaluated at seven days after treatment by measuring the distance from the center of each plot to, first, the most distant point where discoloration of the sunflowers could be found, then at 45° intervals around the center of the plot. The area of discoloration of the sunflowers was calculated, and the area of the direct treatment was subtracted to provide the area affected by the volatility of clomazone.

A second test on Formulation A-1 was carried out in the same manner in a second field of sunflowers, this time with a 44 cm barrel and on a 14x14 meter grid. The total areas affected by clomazone movement from each test site for each test formulation and the standard clomazone 4.0 EC formulation were determined. From these data a percent reduction of area discolored by clomazone as compared to the standard Command® 4 EC was calculated for each test formulation.

A third test, this time with Formulation P, was a series of tests, carried out in different geographic locations having different environmental and soil conditions. At each location a three acre plot was planted with sunflowers. The clomazone formulations were applied to a 10'x10' bare ground plot when the sunflowers had reached the 2-6 leaf stage. Pre-requisite conditions for application were that the soil be moist, but not saturated, to facilitate volatilization. Evaluations were made 7-10 days after application and 10-14 days after the first significant rainfall event by means of the same general method described for the first test. The areas given are totals for all sites; the percent reduction is an average of those from all sites. The test results, given in Table 8, show that Formulation A-1 reduced by one half the area affected by clomazone compared to Command 4 EC, and Formulation P was significantly more effective in reducing volatility.

Efficacy Studies

Seeds of barnyardgrass (*Echinochloa crusgalli*), giant foxtail (*Setaria faberi*), yellow foxtail (*Setaria lutescens*), shattercane (*Sorghum bicolor*), and velvetleaf (*Abutilon theophrasii*) were planted in a 25 cmx15 cmx7.5 cm fiber flat containing topsoil. Each species was planted as a single row in the flat, which contained five rows. There were four replicate flats of plants for each rate of application of test formulation. Stock dispersions of each of the test formulations were prepared by dispersing a sufficient amount of formulation to provide 0.0356 gram of active ingredient in 40 mL of water. From the stock dispersion 20 mL was removed and serially diluted with 20 mL of water to provide application rates of 0.25, 0.125, 0.0625, 0.0313, 0.0156, and 0.0078 kg. a.i./ha. The dispersions of test formulation for each rate of application were then sprayed onto the surface of the soil by a track-sprayer in a sprayhood. Flats were also sprayed as above with the same rates of the standard Command® 4 EC Herbicide. Untreated controls were also included in each test. Upon completion of the spraying the

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flats were placed in a greenhouse, where they were maintained for fourteen days. After this time the test was visually evaluated for percent weed control. The percent weed control data for each test formulation and the Command 4 EC Herbicide formulation was subjected to regression analysis to determine the rate of application that would provide 85% weed control (ED_{85}) of each of the weed species. From these data the relative potencies of the test formulations (the relative potency of the Command 4 EC Herbicide is 1.0) were determined by means of the following ratio:

Formulation Relative Potency = $\frac{\text{Formulation } ED_{85}}{\text{Command Herbicide } ED_{85}}$

The test results shown in Table 9 show relatively poor performance for Formulation E in the greenhouse. As shown below, performance of Formulation E in the field was excellent. The reason for the difference between greenhouse and field performance is not understood. However, the greenhouse performance of Formulation P was excellent, as was performance in the field, as shown below.

In a field test of the efficacy of Formulation A-1 the test formulations were sprayed onto the surface of the soil (preemergence) at an application rate of 1.0 pound a.i./acre in 12.7x30 foot plots planted with cotton and weed seeds. There were four replicate plots for each formulation tested. The test formulation was applied by means of a backpack sprayer, equipped with flat fan spray nozzles, at a delivery volume of 15-20 gallons/acre and at a spray pressure of 28-30 psi. The plots were evaluated for percent weed control at 15 and 30 days after emergence of the plant species in the test. The cotton plants were evaluated for bleaching, stunting, and stand reduction. Test results, given in Table 10, show this CS formulation to be slightly less effective against three of the four test species and essentially equivalent to the 4 EC in effects on cotton. (The similarity in effect on cotton is not unexpected, since this test is the result of direct application and does not involve movement to an adjacent site.)

In a field test of Formulation E the test formulations were sprayed onto the surface of the soil (preemergence) at application rates of 0.125, 0.25, and 0.5 pound a.i./acre in 6.7x12 foot plots planted with eight different plant species. There were four replicate plots for each formulation tested. The test formulations were applied using a backpack sprayer, equipped with four flat fan spray nozzles, at a delivery volume of 20 gallons/acre and at a spray pressure of 25 psi. The plots were evaluated for percent control 20 days after treatment. The data in Table 11 show that this CS formulation at 0.5 pound active ingredient per acre is giving commercial control, defined as at least 80 to 85 percent control of all species, everywhere the standard is giving commercial control, except for shattercane at 0.5 lb/A, which falls slightly below the percentage goal for control.

Table 12 reports results of a field test of Formulation P and the 4 EC formulation in which both formulations were applied at 0.88 lb/A, preemergence. It is apparent that in most cases where the 4 EC formulation is giving commercial control, Formulation P is also. Again, the effect of the encapsulated formulation P on cotton is negligible.

Table 13 reports another field test of Formulation P, again applied preemergence, that shows that at 0.5 lb/A the encapsulated formulation is controlling all species except shattercane.

As noted above, the stabilizers added after encapsulation and curing are thought to have no effect on the volatility or the efficacy of the formulation. They are added to stabilize the formulation and adjust the viscosity. It is preferred that

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each formulation of this invention have a suspensibility of greater than 70%, a viscosity of 1700 to 3800 cps, and a 100 mesh wet screen analysis of greater than 99.95%.

It is understood that there may be variations from the specific embodiments described herein without departing from the spirit or concept of the present invention as defined in the claims. Included in such variations are mixtures in which the encapsulated clomazone of this invention is part of a mixture with one or more other herbicides, e.g., flumeturon or sulfentrazone, whether or not encapsulated.

TABLE I

Preparation of Clomazone Capsule Suspension (CS) Formulations
(Components and Amounts)

Formulation	Weight (grams)					
	A (1.5)	B (2.0)	C (1.5)	D (2.0)	E (2.0)	F (2.0)
Component Aqueous Solution						
Water	430.7	493.00	430.70	493.00	493.00	493.00
PVA	4.0	4.58	4.00	4.58	4.58	4.58
Xanthan Gum	0.3	0.35	0.30	0.35	0.35	0.35
(a.i.)						
Antifoam	1.8	2.06	1.80	2.06	2.00	2.06
(a.i.)						
Isocyanate Solution						
Clomazone	140.0	280.00	140.00	280.00	280.00	280.00
Petroleum Solvent	30.0	60.00	30.00	60.00	60.00	60.00
PMPPi	30.0	60.00	30.00	60.00	60.00	60.00
Amine Solution						
TETA	19.0	38.00	—	—	19.00	9.50
HDA	—	—	19.00	30.00	19.00	28.50
Water	35.0	62.00	31.00	70.00	62.00	62.00
Post Encapsulation Stabilizers						
Smectite Clay in Water	2.5	—	—	—	—	—
Propylene Glycol	14.7	—	—	—	—	—
Xanthan Gum (a.i.)	—	19.60	9.00	18.00	9.00	18.00
	0.3	0.40	1.00	2.00	1.00	2.00
Weight (grams)						
Formulation (lb/gal)	G (2.0)	H (2.0)	I (2.0)	J (2.0)	K (2.0)	
Component Aqueous Solution						
Water	493.00	493.00	493.00	493.30	493.00	
PVA	4.6	4.6	4.58	4.58	4.58	
Xanthan Gum (a.i.)	0.4	0.4	0.35	—	0.35	
Antifoam (a.i.)	2.1	2.06	2.06	2.06	2.06	
Isocyanate Solution						
Clomazone	280.0	280.00	280.00	280.00	280.00	
Petroleum Solvent	60.0	60.00	60.00	60.00	60.00	
PMPPi	60.0	60.00	60.00	60.00	60.00	
Amine Solution						
EDA	—	—	7.6	7.6	—	
TETA	—	—	30.4	30.4	—	
DETA	11.20	19.00	—	—	38.00	
HDA	19.00	19.00	—	—	—	
Water	69.8	62.00	62.00	62.00	62.00	
Post Encapsulation Stabilizers						
Smectite Clay in Water	—	—	—	—	—	

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TABLE 1-continued

Preparation of Clomazone Capsule Suspension (CS) Formulations (Components and Amounts)					
5	Propylene Glycol	—	41.00	19.60	19.60
	Xanthan Gum (a.i.)	—	1.00	0.40	0.40
<p>PVA - Airvol @ 203 polyvinyl alcohol.</p> <p>Xanthan gum - Kelzan @ M and Kelzan S xanthan gums differ in that S has been surface treated to improve ease of dispersion. M was used in all cases except post encapsulation in Formulations A, C, D, F, and H.</p> <p>Antifoam - Dow Corning @ 1500 is 100% polydimethyl siloxane. Dow Corning 1520 is a 20% solution; amount shown is active ingredient (a.i.). 1500 was used in Formulations A and C; 1520 in the others.</p> <p>Petroleum solvent - Aromatic 200, a mixture of C₉-C₁₅ aromatic hydrocarbons, flash point 95° C. That used in Formulation A was naphthalene depleted.</p> <p>PMPPi - Mondur @ MR polymethylene polyphenyl isocyanate.</p> <p>TETA - triethylenetetramine.</p> <p>HDA - 1,6-hexanediamine.</p> <p>Smectite clay - Veegum @ Ultra clay consisting of magnesium aluminum silicates with titanium dioxide and cristobalite present.</p> <p>EDA - ethylenediamine.</p> <p>20 DETA - diethylenetriamine.</p>					

TABLE 2

Clomazone Capsule Suspension (CS) Formulations (Components and Weight/Weight Percents)						
25	Formulation	Percent (wt/wt)				
	(lb/gal)	A (1.5)	B (2.0)	C (1.5)	D (2.0)	E (2.0)
	Component					
30	Clomazone	19.77	27.45	20.09	27.45	27.72
	Encapsulating Polymer					
	PMPPi	4.24	5.88	4.31	5.88	5.94
	HDA	—	—	2.72	2.94	1.88
35	TETA	2.68	3.73	—	—	1.88
	Polyvinyl Alcohol	0.56	0.45	0.57	0.45	0.45
	Petroleum Solvent	4.24	5.88	4.31	5.88	5.94
	Polydimethyl Siloxane-Antifoam Agent	—	—	—	—	—
40	Xanthan Gum	0.08	0.07	0.19	0.23	0.13
	Viscosity Modifier/Stabilizer					
45	Propylene Glycol	—	1.92	1.29	1.77	0.89
	Stabilizer					
	Smectite Clay	0.35	—	—	—	—
50	Viscosity Modifier					
	Water	67.83	54.42	66.26	55.20	54.95
	Total	100.00	100.00	100.00	100.00	100.00
55	Formulation	Percent (wt/wt)				
	(lb/gal)	G (2.0)	H (2.0)	I (2.0)	J (2.0)	K (2.0)
	Component					
60	Clomazone	28.00	26.7	27.45	27.45	27.45
	Encapsulating Polymer					
	PMPPi	6.00	5.70	5.88	5.88	5.88
	EDA	—	—	0.75	0.75	—
	TETA	—	—	2.98	2.98	—
	DETA	1.12	1.80	—	—	3.73

TABLE 2-continued

5	HDA	1.90	1.80	—	—	—
	Polyvinyl Alcohol	0.46	0.44	0.45	0.45	0.45
	Petroleum Solvent	6.00	5.70	5.88	5.88	5.88
	Polydimethyl	0.21	0.20	0.20	0.20	0.20
	Siloxane-					
10	Antifoam Agent					
	Xanthan Gum-	0.04	0.13	0.07	0.04	0.07
	Viscosity					
	Modifier/					
	Stabilizer					
	Propylene	—	4.67	1.92	1.92	1.92
15	Glycol					
	Stabilizer					
	Water	<u>56.27</u>	<u>52.86</u>	<u>54.42</u>	<u>54.45</u>	<u>54.42</u>
	Total	100.00	100.00	100.00	100.00	100.00

TABLE 3

Large Scale Preparation of Clomazone CS Formulations (Components and Amounts)			
Formulation (lb/gal)	Weight (lbs)		
	A-1 (1.5)	E-1 (2.0)	P (3.0)
Component			
Aqueous Solution			
Water	222.85	284.20	274.4
PVA	2.000	5.24	5.05
Xanthan Gum	0.300	0.21	0.22
Antifoam	0.900	2.38	4.30
Isocyanate Solution			
Clomazone	70.000	161.34	289.8
Petroleum Solvent	15.000	34.75	31.2
PMPPi	15.000	34.75	62.5
Amine Solution			
TETA	9.500	10.97	
HDA	—	10.97	
DETA	—	—	40.0
Water	17.500	40.50	
Post Encapsulation Additives			
Propylene Glycol	—	35.70	39.8
Xanthan Gum	—	1.19	26.2*
Smectite Clay	1.250	—	—
Bactericide A ¹	0.009	—	—
Bactericide B ²	0.177	—	—
Bactericide C ³	—	—	0.4
Na Naphthalene Sulfonate ⁴	—	—	5.3
Concentrated Aqueous HCl	—	—	22.33
Amphoteric Surfactant ⁵	—	—	26.0

¹Dowcide ® A (o-phenylphenate tetrahydrate)²¹ Legend ® MK (mixture of 2-methyl-4-isothiazolin-3-ones)³Proxel® (1,2-benzisothiazolin-3-one)

⁴Sodium salt of sulfonated naphthalene condensate

⁵Mirataine™ H2C-HA (sodium lauriminodipropionate)

*as a 1.9 wt % dispersion.

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TABLE 4

Large Scale Clomazone CS Formulations
(Components and Weight/Weight Percents)

Formulation	Percent (wt/wt)		
	A-1	E-1	P
Component			
Clomazone Encapsulating Polymer	19.74	25.93	35.02
PMPPi	4.23	5.59	7.55
HDA	—	1.76	—
TETA	2.68	1.76	—
DETA	—	—	4.83
Polyvinyl Alcohol	0.56	0.84	0.61
Petroleum Solvent	4.23	5.59	3.77
Polydimethyl Siloxane-Antifoam Agent	0.25	0.38	0.53
Xanthan Gum-Viscosity Modifier/Stabilizer	0.09	0.23	0.09
Propylene Glycol Stabilizer	—	5.74	4.81
Smectite Clay-Viscosity Modifier	0.37	—	—
Bactericides	0.05	—	0.05
Na Naphthalene Sulfonate Condensate	—	—	0.65
Concentrated Aqueous Hcl	—	—	2.70
Amphoteric Surfactant	—	—	0.94
Water	67.80	52.18	38.45
Total	100.00	100.00	100.0

TABLE 5

Unsatisfactory Clomazone CS Formulations
(Components and Weight/Weight Percents)

Formulation	Percent (Wt/Wt)			
	L	M	N	O
Component				
Clomazone Encapsulating Polymer	20.38	30.43	20.38	27.45
PMPPi	—	—	4.37	5.88
TDI	4.37	1.73	—	—
TETA	2.77	—	2.77	—
DETA	—	0.73	—	3.73
EDA	—	0.15	—	—
Polyvinyl Alcohol	0.58	2.72	0.58	0.45
Petroleum Solvent	4.37	—	4.37	5.88
Polydimethyl Siloxane Antifoam Agent	0.26	0.28	0.26	0.20
Xanthan Gum Viscosity Modifier/Stabilizer	0.04	—	—	0.04
Propylene Glycol Stabilizer	—	—	—	1.92
Water	67.23*	63.96	67.27*	54.45*
Total	100.00	100.00	100.00	100.00

TDI is toluene diisocyanate
DETA is diethylenetriamine
EDA is ethylenediamine
*Ten mL of a 10% solution of xanthan gum in propylene glycol was added to stabilize the formulation after it was prepared.

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TABLE 5a

Unsatisfactory Clomazone CS Formulations
(Components and Weight/Weight Percents)

Formulation	Weight (g)		Percent (Wt/Wt)	
	V	W	V	W
Component				
Clomazone	300.0	300.0	34.9	49.0
Encapsulating Polymer				
PMPPi	22.5	22.5	2.6	3.7
HDA (40%)	24.8	24.8	2.9	4.0
Reax 88B ®	11.6	5.7	1.3	0.9
Ethylene Glycol Stabilizer	25.7	25.7	3.0	4.2
Water	476.0	234.0	55.3	38.2
Total	860.6	612.7	100.00	100.00

HDA is 1,6-hexanediamine.
Reax 88B ® is a sodium lignosulfonate.

TABLE 6

Average Particle Size of Microcapsules in Clomazone CS Formulations

Formulation	Average Particle Size (µm)	Formulation	Average Particle Size (µm)
A	26	J	11
B	21	K	17
C	16	L	14
D	18	M	2
E	15	N	9
F	15	O	7
G	23	P	14
H	12	V	21
I	12	W	17

Particle size was determined using a Malvern Master Sizer MS 20.

TABLE 7

Volatility of Clomazone from CS Formulations as Compared to the Volatility of Clomazone from the Standard, Command ® 4 EC Herbicide

Formulation	Micrograms of Clomazone Collected	Percent of 4.0 EC
A	28	32
B	30	33
C	17	19
D	20	22
E	8	8
F	9	10
G	15	14
H	13	14
I	21	15
J	23	17
K	24	17
L	81	91
M	•	110
N	56	62
O	22	16
P	14	14
V	110	103
W	126	114
Standard 4.0 EC	90-93	100

*Volatility determined by a different test method.

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TABLE 8

Volatility Effect of Clomazone CS Formulations Compared to
Command @ 4 EC Herbicide on Sunflowers in Field Studies

Formulation (Test No.)	Area of Discolored Sunflowers (cm ²)	Percent Reduction in Area Discolored by Volatility
A-1 (1)	6578	49.0
Command 4 EC	12904	
A-1 (2)	17449	52.8
Command 4 EC	37004	
P	256334	67.5
Command 4 EC	788721	

TABLE 9

Relative Potency of Clomazone CS Formulations Compared to
Command @ 4 EC Herbicide against Weed Species
in Greenhouse Studies

Relative Potency						
Formulation	Barnyard-grass	Giant Foxtail	Yellow Foxtail	Shatter-cane	Green Foxtail	Velvet-leaf
A	0.70	0.54	0.35	0.66	—	0.69
D	0.50	0.59	1.02	0.40	—	0.36
E	0.19	0.28	•	•	—	0.34
P	0.63	0.54	—	0.95	0.95	0.90

*Too small to measure at rate tested.

TABLE 10

Efficacy of Clomazone CS Formulation A-1 Compared to
Command @ 4 EC Herbicide against Weeds in Field Studies

Percent Control 15 DAE ¹ and 30 DAE								
Formulation	Johnson-grass		Bermuda-grass		Pitted Morningglory		Sicklepod	
	15	30	15	30	15	30	15	30
A-1	68	54	0	1	72	54	26	—
4.0 EC	85	56	20	55	66	70	21	—

Effects on Cotton

Percent Bleaching				Stand Reduction	Stunting
	15	30			
A-1	0.7	0.5		none	none
4.0 EC	0.7	0.7		none	none

¹DAE is days after emergence of the test plant species.
Rate of application is 1.0 pound a.i./acre.

TABLE 11

Efficacy of Clomazone CS Formulation E Compared to
Command @ 4 EC Herbicide
against Certain Weed Species in Field Studies

Percent Control Rate of Application (lb. ai/A) ¹						
Plant Species	0.5		0.25		0.125	
	E	4 EC	E	4 EC	E	4 EC
Barnyardgrass	100	100	98	99	91	97
Giant Foxtail	100	100	98	98	95	96
Yellow Foxtail	95	93	50	57	50	35

T0150

T0151

T0152

T0153

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TABLE 11-continued

Efficacy of Clomazone CS Formulation E Compared to Command @ 4 EC Herbicide against Certain Weed Species in Field Studies							
Percent Control Rate of Application (lb. ai/A) ¹							
Plant Species	0.5		0.25		0.125		
	E	4 EC	E	4 EC	E	4 EC	
Green Foxtail	99	100	83	95	53	68	
Shattercane	73	90	33	53	33	35	
Johnsongrass	100	100	93	97	85	93	
Spring Wheat	55	60	18	26	8	9	
Velvetleaf	100	100	93	96	85	93	
Grass	95	97	77	83	68	71	
Average ²							

¹Formulations applied to the plots preemergence.

²Velvetleaf and Spring Wheat are not included in the grass average. Percent control ratings were determined 20 days after treatment.

TABLE 12

Efficacy of Clomazone CS Formulation P Compared to
Command @ 4 EC Herbicide against Weeds in Field Studies

Percent Control							
Plant Species	15 DAT		30 DAT		60 DAT		
	P	4 EC	P	4 EC	P	4 EC	
Velvetleaf	95.0	95.0	97.5	97.55	—	—	
Prickly Sida	89.3	90.5	83.6	90.7	77.3	88.5	
Spotted Spurge	—	—	95.0	98.0	—	—	
Cocklebur	58.8	72.5	58.8	59.4	87.5	93.5	
Broadleaf	100.0	100.0	100.0	100.0	95.0	95.0	
Signalgrass	—	—	96.0	97.0	—	—	
Seedling	—	—	—	—	—	—	
Johnsongrass	—	—	95.5	99.0	100.0	100.0	
Large Crabgrass	—	—	—	—	—	—	
Pitted	93.0	95.2	82.9	89.5	78.4	88.5	
Morningglory	—	—	—	—	—	—	
Ivyleaf	92.1	95.0	88.0	91.0	57.0	77.0	
Morningglory	—	—	—	—	—	—	
Entire	73.9	70.9	73.9	71.6	66.9	73.0	
Morningglory	—	—	—	—	—	—	
Spp.	—	—	95.7	99.3	99.0	99.0	

Effects on Cotton (Percent)

Formulation	15 DAT		30 DAT		60 DAT	
	P	4 EC	P	4 EC	P	4 EC
Stand Reduction	0	0	0	0	0	0
Stunting	0.5	0.2	1.1	3.0	0	0
Discoloration	1.8	5.9	1.7	4.9	0	0.2

DAT is days after treatment.

Rate of application for both formulations is 0.88 pound a.i./acre.

663270 346200

70160

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Percent control ratings were determined 18 days after treatment.